

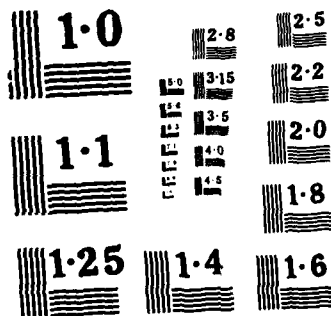
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This report presents experimental results of the vibrational relaxation of DF ( $2 < v < 4$ ) and DF ( $9 < v < 12$ ). The fast flow infrared chemiluminescence method was used to determine vibrational relaxation rate constants for the processes DF ( $2 < v < 4$ ) + CO, HF, DF, N<sub>2</sub>O, CF<sub>4</sub>, and SF<sub>6</sub> and DF ( $9 < v < 12$ ) + N<sub>2</sub>, CO, HF, DF, CO<sub>2</sub>, and N<sub>2</sub>O. These are the first measurements of relaxation rate constants for the high vibrational states of DF. They are combined with low v-level data in order to gain additional insight into fundamental energy transfer questions such as the origin of the unusually strong v-dependence of

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DF VIBRATIONAL RELAXATION

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ONR Final Report  
DF Vibrational Relaxation

INTRODUCTION

Studies of the vibrational relaxation of highly excited DF carried out at the University of Pittsburgh in support of the Navy's pulsed DF chemical laser program have been successfully completed. Vibrational relaxation rate constants were determined for  $DF(v = 2-4)$  by the quenchers  $Q = CO, HF, DF, N_2O, CF_4$ , and  $SF_6$  and for  $DF(v = 9-12)$  by  $Q = N_2, CO, HF, DF, CO_2$ , and  $N_2O$  using the fast flow infrared chemiluminescence technique.<sup>1-3</sup> This technique is a variant of an earlier chemiluminescence method used previously to measure vibrational relaxation rate constants for  $HCl (v \leq 7)$ <sup>4,5</sup> and  $HF(v \leq 7)$ .<sup>6-8</sup>

While interest in chemical lasers has focussed attention on vibrationally excited hydrogen fluoride and its deuterated analog, the general problem of collisional energy transfer also warrants additional experimental and theoretical study. For example, studies of  $HF(v)$  report very efficient relaxation of the high vibrational states by most quenchers, which when combined with low  $v$ -level data indicate unusually strong  $v$ -dependences.<sup>6,7,9-11</sup> The latter effect may be qualitatively attributed to the influence of the large anharmonicity and dipole moment of HF on the intermolecular interaction potential. For the case of HF self-relaxation, the inverse temperature dependences of the total rate constants indicate control of the collision dynamics by long range forces.<sup>12</sup> According to both experiment and theory,<sup>8,10,13-16</sup> the self-relaxation rates are increasingly dominated by vibrational to rotational and translational (V-R,T) energy

transfer for higher vibrational levels, while vibrational to vibrational (V-V) energy exchange is only important for the lower levels.

This report presents new results pertaining to the step-wise relaxation of DF(v) produced by the so-called "hot" and "cold" reactions,  $D + F_2 \rightarrow DF(v \leq 13) + F$  and  $F + D_2 \rightarrow DF(v \leq 4) + D$ . Combined with some of our earlier data, this constitutes a complete survey of all four combinations of the XF(v) + XF system, (X = H, D), for higher v. In addition, useful comparisons can be drawn between the vibrational relaxation of energetically comparable states of HF(v) and DF(v) by collision partners covering a range of acceptor frequencies and structures.

The majority of previous experimental studies of DF vibrational relaxation have determined rate constants for  $v = 1$ , including the temperature dependence for some quenchers.<sup>17</sup> A few isolated measurements of  $v = 2, 3$ , and 4 have been reported,<sup>18-20</sup> as well as chemiluminescence results of Poole and Smith<sup>21</sup> for  $DF(3 \leq v \leq 5)$  with several collision partners. Theoretical calculations have been carried out for  $DF(1 \leq v \leq 5) + CO_2$ ,<sup>22</sup>  $DF(v \leq 7) + HF(v = 0)$ ,<sup>23</sup> and  $DF(v \leq 7) + DF(v = 0)$ .<sup>16,24,25</sup>

This report also includes results for the initial, unrelaxed vibrational state distributions of product DF(v) from the  $F + D_2$  and  $D + F_2$  reactions in experiments in which no quencher, Q, was added. Under the experimental conditions used in our fast flow reactor, the rotational distribution can be assumed to be thermalized while the vibrational distribution remains unrelaxed, as previously discussed.<sup>1</sup> Our measurement of the initial DF(v) distribution from the "hot"  $D + F_2$  reaction is particularly important because of the substantial disagreement between the previous studies.<sup>26,27</sup>



## EXPERIMENTAL

The apparatus and procedure have been previously described.<sup>1,4</sup> A dilute flow of D or F atoms, produced by passing D<sub>2</sub> or CF<sub>4</sub> mixtures in He or Ar through a pulsed (13 Hz) microwave discharge, was rapidly mixed with, respectively, an F<sub>2</sub> or D<sub>2</sub> flow in the field of view of an infrared spectrometer. Typical reagent concentrations in the rapidly pumped flow tube (P ~ 0.7 torr and v ~ 90 m/s) were [D] ~ 2-6 x 10<sup>12</sup> cm<sup>-3</sup> and [F<sub>2</sub>] ~ 3 x 10<sup>13</sup> cm<sup>-3</sup> for the D + F<sub>2</sub> generating reaction and [F] ~ 1 x 10<sup>11</sup> cm<sup>-3</sup> and [D<sub>2</sub>] ~ 3 x 10<sup>13</sup> cm<sup>-3</sup> for the F + D<sub>2</sub> reaction. The spectrometer consisted of a liquid N<sub>2</sub> cooled circularly variable filter (CVF) and InSb detector. In the low v-level experiments, the fundamental emission of DF(v) was scanned, while higher v-state data were obtained from first-overtone scans, since the fundamental emission of DF(v ≥ 9) is beyond the CVF cutoff of λ = 4.5 μm.

Calibrated mass flowmeters were used to measure the larger inert gas flows in the main flow tube (φ<sub>He</sub> ≈ 140 sccs) and discharge sidearm (φ<sub>He</sub> ≈ 10 sccs and φ<sub>Ar</sub> ≈ 2.5 sccs). The quencher gas was introduced ~16 cm upstream of the reaction zone at concentrations of 10<sup>13</sup> - 10<sup>16</sup> cm<sup>-3</sup>. Typically, six or more concentrations were run in each experiment set with two or three such sets run for each quencher. Each experiment consisted of quencher-free spectra interspersed between partially relaxed spectra to monitor the stability of the reaction conditions.

For low v-level experiments with relatively inefficient quenchers the pressure in the main flow tube was increased to about 1.5 torr, and quencher flows approached ~10% of

the total flow. As previously discussed,<sup>5</sup> a complication arises in these instances. As more quencher is added, the total pressure increases proportionally less than the total flow, decreasing all concentrations. For large  $[Q]$  this dilution becomes nonnegligible, and the quenching rate appears to be enhanced. This effect was experimentally minimized by corresponding decreases in the helium carrier gas flow rate.

The data acquisition system was based on phase sensitive detection coupled with digital integration of the emission intensity. Modifications allowed for real-time data transfer to a microcomputer via an RS232 serial line. The intensity at each wavelength increment was integrated for  $\sim 7.6$  s.

At the completion of each experiment, the spectra were fit using a non-linear least squares routine which compares experimental with calculated intensities.<sup>1</sup> The band intensity per unit population was calculated using the Dunham coefficients of Johns and Barrow<sup>28</sup> and the Einstein emission coefficients,  $A_{v'J'-v''J''}$  made available to us by Setser and Oba,<sup>29</sup> which we gratefully acknowledge. In order to insure a fair comparison with our earlier HF results,<sup>6,7</sup>  $A$  values were also obtained for HF from Setser and Oba.<sup>29</sup> These Einstein coefficients were within 2% of those calculated earlier<sup>30,31</sup> and yield relaxation rate constants identical to those reported in References 6 and 7.

Vibrational relaxation rate constants  $k_{v,v-1}^Q$  were determined using a modified Stern-Volmer analysis assuming stepwise,  $\Delta v = -1$ , collisional relaxation. The use of this approximation has been previously discussed,<sup>7</sup> and the resulting equation is:

$$\frac{N_v^*}{N_v} = \frac{k_p}{k_\ell} \sum_{m=1}^{m_{\text{mix}}} \left( \frac{N_v^* - N_v}{N_v} \right) = 1 + \frac{k_{v,v-1}^Q [Q]}{k_\ell}$$

In this method, advantage is taken of the short average residence time of DF(v) in the field of view,  $\sim 2 \times 10^{-4}$  s, which insures that the reference rate constant,  $k_\ell$ , is dominated by the fast pumping term  $k_p \sim 5 \times 10^3 \text{ s}^{-1}$ . Under slow flow conditions at higher pressure  $k_p \sim 2000 \text{ s}^{-1}$  still represents the major loss process in comparison to radiative and wall losses.

## RESULTS AND DISCUSSION

## Initial Vibrational State Distributions

The following average relative vibrational distribution for  $DF(v=1,4)$ , was determined for the  $F + D_2$  reaction: 0.24 : 0.49 : 1.00 : 0.70. (The  $[F]$  ranged from  $0.5$  to  $4.0 \times 10^{11} \text{ cm}^{-3}$ , and the  $[D_2]$  was varied between  $0.04$  and  $10.0 \times 10^{13} \text{ cm}^{-3}$ .) Three previous studies (see Table 1), two using the arrested relaxation method<sup>32,33</sup> and one using the chemiluminescence mapping method,<sup>27</sup> give similar relative populations and average vibrational energy disposal. Bittenson et al.<sup>27</sup> report a slightly less relaxed distribution at higher  $v$ . The relative  $v = 1$  concentration determined by Polanyi and Woodall<sup>32</sup> is estimated by extrapolation from higher levels, since no detectable  $v = 1$  emission was observed in their experiments. The good overall agreement among these studies is taken to indicate the absence of unexpected relaxation processes in this work, which could potentially introduce errors into our quenching rate constants.

Comparison of the  $F + D_2$  distribution with results for the nearly isoenergetic  $F + H_2$  reaction, 0.29 : 1.00 : 0.52 for  $v = 1-3$ ,<sup>7</sup> indicate a similar distribution when plotted in terms of vibrational energy of the product  $HX$ . The average vibrational energy disposals are essentially identical,  $\langle f_v \rangle = 0.67$ . The extremely efficient channeling of energy into vibration is attributed to mixed energy release on a repulsive hypersurface; the  $H/D$  product is ejected as the new  $HF/DF$  bond is still being formed.<sup>32</sup> Studies of other isotopic pairs of reactions, such as  $Cl + HI/DI$ ,<sup>34</sup>  $H/D + Cl_2$ ,<sup>35</sup>  $F + HCl/DCl$ ,<sup>36</sup>  $F + HBr/DBr$ ,<sup>36,37</sup> and  $F + NH_3/ND_3$ <sup>38</sup> have also found roughly the same average energy disposal into internal and translational product excitation, consistent with results of trajectory calculations.

The initial DF(v) distribution of the  $D + F_2$  reaction was studied over a wide range of reactant concentrations,  $[D] \sim (0.05 - 3.50) \times 10^{13} \text{ cm}^{-3}$  and  $[F_2] \sim (0.40 - 4.5) \times 10^{13} \text{ cm}^{-3}$ . Emission was observed from  $v = 3$  to 13 with the peak in the distribution at  $v = 9$ . Comparison of our results (see Table 2) with the very narrow distribution Bittenson et al.<sup>27</sup> obtained using the chemiluminescence mapping method suggests that errors exist in these authors' study, probably due to signal handling problems similar to those earlier encountered in Tardy et al.'s<sup>39</sup>  $H + F_2$  experiments. Whereas a substantially smaller  $\langle f_v \rangle$  value, 0.64, in closer agreement with our  $\langle f_v \rangle$  of 0.62, was obtained by Jonathan et al.'s<sup>26</sup> measured relaxation study, the peak of their distribution occurs at  $v = 10$  versus ours at  $v = 9$ . The reason for this disagreement, which is outside the experimental error, remains unclear. Although Jonathan et al.<sup>26</sup> used different Dunham coefficients and Einstein A values in their spectral analysis, this choice of parameters cannot account for all of the discrepancy.

A plot of the DF(v) initial relative distribution on an equal energy scale with that of HF(v) from the  $H + F_2$  reaction<sup>6</sup> shows no overlap between the two sets of results, particularly in terms of the peak in the distribution, which is displaced to higher energy for DF(v). A faster falloff is found for the lower v levels of DF, as well as significant vibrational state population at energies closer to the thermochemical limit. Indeed, for the  $D + F_2$  reaction we find  $\langle f_v \rangle \sim 0.64$  while for  $H + F_2$ ,  $\langle f_v \rangle \sim 0.53$ , in contrast to the nearly equal  $\langle f_v \rangle$ 's observed for the  $F + H_2/D_2$  reaction pair.

For the  $H/D + F_2$  reactions, the differing energy disposals can be rationalized as arising from the "light-atom anomaly."<sup>40</sup> Briefly stated, light attacking atoms favor energy

disposal into translational, at the expense of vibrational, excitation. The failure of this explanation in the case of  $H/D + Cl_2$ , which exhibits a lower, isotopically invariant  $\langle f_v \rangle = 0.40$ , should not be cause for undue alarm. Polanyi<sup>40a</sup> has pointed out that the product vibrational energy disposal is most sensitive to details of the potential energy hypersurface for the light + heavy-heavy combination. Further, we know that the  $H + F_2$  surface is quite different from  $H + Cl_2$  surface, owing to the very short range repulsive interaction between the separating F atoms, reflected in the smaller bond dissociation energy of  $F_2$ .<sup>41-43</sup>

Our results are also consistent with the quantum mechanical calculations by Connor et al.<sup>44</sup> of reaction probabilities for the reaction  $X + F_2 \rightarrow XF + F$ ,  $X = Mu, H, D$ , and  $T$ . The calculated  $\langle f_v \rangle$ 's increased in the order  $Mu < H < D < T$  as expected according to the light-atom anomaly concept, although the increase from the H to D reaction, 0.56 to 0.62, is not quite as large as our data indicate.

#### Quenching Rate Measurements

Quenching rate constants are listed in Tables 3-5 along with the corresponding relaxation probabilities,  $P$ , and rotationless energy defects,  $\Delta E_{v-v'}$ . The major uncertainty in the absolute rate constants is the value of  $k_{\text{L}}$  which is dominated by the fast pumping term and has an uncertainty of about 20%. The scatter of the data contributes another 5-10% to the uncertainty. The relaxation probability,  $P$ , is defined as  $k_{v,v-1}^Q/k_{LJ}$ , where  $k_{LJ} = \pi d_{AB}^2 c \Omega^{(2,2)}$  is the Lennard-Jones collision rate. The average collision diameter,  $d_{AB} = (d_A + d_B)/2$ , and interaction potential,  $\epsilon_{AB} = (\epsilon_A \epsilon_B)^{1/2}$ , were obtained from

transport properties<sup>45</sup> and the collision integrals  $\Omega^{(2,2)}$  from Hirschfelder, Curtiss, and Bird.<sup>46</sup> The DF vibrational quanta  $\nu_{1,0}$ ,  $\nu_{2,1}$ ,  $\nu_{3,2}$ , and  $\nu_{4,3}$  are 2907, 2815, 2726, and 2639  $\text{cm}^{-1}$ , respectively, and the quanta  $\nu_{9,8}$ ,  $\nu_{10,9}$ ,  $\nu_{11,10}$ , and  $\nu_{12,11}$  are 2223, 2143, 2062, and 1982  $\text{cm}^{-1}$ , respectively. A positive  $\Delta E_{V-V}$  indicates an exoenergetic energy transfer. Although emission from  $v = 13$  was observed in the  $\text{D} + \text{F}_2$  experiments, the small, uncertain population precluded relaxation rate measurements. However, the small cascade contribution into lower  $v$  states was included in the analysis.

In reference to comparisons with  $\text{HF}(v)$  relaxation rate constants, it should be pointed out that the energy range of the populated  $\text{DF}(v)$  levels is larger than that of  $\text{HF}(v)$ . For instance,  $\text{HF}(v = 7)$  carries 69.37  $\text{kcal mol}^{-1}$ , whereas  $\text{DF}(v = 12)$  carries 83.52  $\text{kcal mol}^{-1}$  of (rotationless) vibrational energy. The  $v = 10$  state of  $\text{DF}$  (71.96  $\text{kcal mol}^{-1}$ ) is closest to the highest  $\text{HF}(v)$  state,  $v = 7$ , for which relaxation rate constants have been measured.

Quenching of  $\text{DF}(9 \leq v \leq 12)$  and  $\text{HF}(5 \leq v \leq 7)$  by  $\text{HF}(v = 0)$  and  $\text{DF}(v = 0)$

The relaxation rate constants for all four combinations of  $\text{HF}(5 \leq v \leq 7)/\text{DF}(9 \leq v \leq 12)$  with ground state  $\text{HF}/\text{DF}$  are in the range  $1.4$  to  $5.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , corresponding to probabilities per gas-kinetic (Lennard-Jones) collision of 0.47 to 1.72 (see Table 3). Except for  $\text{HF}(v) + \text{HF}(0)$ , which has been discussed elsewhere,<sup>6-8</sup> there are no other reported relaxation rate measurements. The usual power law fit,  $\log k_{v,v-1}^Q$  vs.  $\log v$ , shows a surprisingly similar  $v$  dependence,  $n \sim 2.6$ - $2.8$ , for all four processes, in spite of their widely different  $\Delta E_{V-V}$  values. Furthermore, the rate constants are independent of the magnitude or sign of the vibrational (V-V) energy defect, indicating that these processes involve V-R,T energy transfer.

In the unsymmetrical  $DF(v) + HF$  and  $HF(v) + DF$  relaxation reactions, it was possible to assess directly the contribution of V-V processes by looking for IR emission from the  $v = 1$  state of the quencher molecule. For the  $DF(v) + HF$  energy transfer, no  $HF(v = 1)$  emission was observed, yielding an upper limit of 1-2% for the total V-V channel. Since the  $\Delta v = -1$  channel for  $DF(v) + HF$  is highly endothermic, this upper limit pertains to  $\Delta v = -2$  relaxation, which is nearly resonant for  $DF(v = 12)$ . For  $HF(v) + DF$  relaxation, although the V-V channels are nearly resonant to mildly exothermic, the average V-V fraction is  $\leq 5\%$ .

Comparing the relaxation rate constants for the nearly isoenergetic  $HF(v = 7)$  and  $DF(v = 10)$ , it is seen that  $HF(v) + HF$  is the largest,  $HF(v) + DF$  and  $DF(v) + HF$  are intermediate, and  $DF(v) + DF$  is the smallest, paralleling the trend in B rotational constants of the product species. Attempts to rationalize this correlation are fraught with danger, because of the different amounts of energy transferred and the different  $\Delta J$  values required to absorb this energy into rotation of the products. Given these differences, the most striking features of the results are the extremely large and similar rate constants, suggesting that these reactions are entrance-channel controlled, the details of the energy transfer mechanism having little effect on the observed rate constant.

Quenching of  $DF(2 \leq v \leq 4)$  by  $HF(v = 0)$  and  $DF(v = 0)$

As Table 4 shows, these are fairly efficient processes, with the efficiency increasing rapidly with  $v$ . Interestingly, for both  $v = 3$  and 4, the rate constants for  $Q = HF$  and  $DF$  are very similar but, for  $v = 2$ ,  $DF$  is substantially more efficient than  $HF$ . Comparison of



the  $Q = HF$  values with previous studies<sup>18,19,21,47</sup> indicates poor agreement especially for  $v = 3$  and 4, due, in part, to uncorrected secondary processes<sup>21,47</sup> and V-V coupling in the earlier work.<sup>18</sup> Previous measurements for DF self-relaxation are only available for  $v = 2$  where the agreement is very good among the three laser studies.<sup>48-50</sup> Our value is slightly smaller; however, there is a large uncertainty in our  $k_{2,1}^{DF}$  due to cascade effects.

For the  $DF(2 \leq v \leq 4) + DF(v = 0)$  reactions, the incorrect dependence of the Lambert-Salter plot for V-V energy exchange is suggestive of a V-R,T contribution; however, the relatively small  $\Delta E_{V-V}$ 's may lead to a significant V-V fraction due to rotational bridging effects, similar to behavior found experimentally for HF self-relaxation.<sup>8</sup> The deviations of  $k_{2,1}^{DF}$  and  $k_{3,2}^{DF}$  from the power law correlation ascribed to V-R,T deactivation of the higher vibrational states may be a further indication of the opening up of the V-V channel. If this is the case, then the V-V channel should account for about 85% of the relaxation from  $v = 2$ .

In contrast, the  $Q = HF$  energy transfer mechanism is likely to principally involve V-R,T processes since V-V deactivation is highly endothermic. The semi-empirical power law correlation gives a good fit, with  $n = 2.6$ , over the combined ranges  $v = 2-4$  and  $v = 9-12$ . This  $v$ -dependence is similar to that determined for other quenchers of the low  $v$  states of DF.<sup>3</sup>

The general conclusions discussed above are in overall agreement with the results of a kinetic model<sup>15</sup> and several trajectory calculations.<sup>16,24,25</sup> The rotational nonequilibrium model of Wilkins and Kwok,<sup>15</sup> designed to simulate quenching rate

constants, was based on their previous trajectory results and suggests that intramolecular energy conversion is a significant factor in the overall energy transfer mechanism. In particular, the key process for DF self-relaxation was determined to be V-R energy transfer. The agreement of several sets of absolute relaxation rate constants obtained from trajectory studies<sup>16,24,25</sup> with experiment is generally fair, the best comparison being with the results of Coltrin and Marcus.<sup>16</sup> This is attributed to several factors, including their choice of intermolecular potential energy surface, their use of the Morse (i.e. an anharmonic) vibrational potential, and their inclusion of vibrational-rotational coupling. Although the three trajectory studies differ in the detailed treatment of the collisional energy transfer process, they all found increasing V-R,T rate constants with increasing vibrational quantum number and a significant V-V pathway only for the lower vibrational levels. For example, Coltrin and Marcus<sup>16</sup> report V-V fractions between 88 and 97% for  $2 \leq v \leq 4$  but only a 12% contribution at  $v \approx 7$ , which they attribute to both increasing vibrational frequency mismatch and increasing endothermicity.

Quenching of DF( $2 \leq v \leq 4$ ) by Q = CO, N<sub>2</sub>O, CF<sub>4</sub>, and SF<sub>6</sub> and of DF( $9 \leq v \leq 12$ ) by Q = N<sub>2</sub>, CO, CO<sub>2</sub>, and N<sub>2</sub>

Comparison of the quenching rate constants for the lower v-levels with those for  $v = 9-12$  indicates a strong v-effect similar to that found for HF vibrational relaxation.<sup>6,7</sup>

The collisional relaxation processes are particularly efficient for the high vibrational states as summarized in Table 5. The smaller absolute rate constants determined for  $v = 2-4$  partly reflect larger energy gaps for V-V energy transfer.

To the authors' best knowledge, these are the first measurements of  $\text{DF}(9 \leq v \leq 12)$  relaxation by the collision partners  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$ . There are several measurements<sup>17</sup> of  $k_{1,0}$  for  $\text{CF}_4$  and  $\text{SF}_6$ , but none for higher  $v$  states. For  $\text{DF}(v \leq 4) + \text{CO}$ , the results of Poole and Smith<sup>21</sup> are available for comparison; however, their rate constants for  $v = 3$  and  $4$  are lower by about a factor of four due to secondary relaxation processes similar to those in their  $\text{HF}(v)$  relaxation work. Due to the inefficiency of  $\text{SF}_6$  as a collisional relaxation partner, we were only able to determine  $k_{4,3}^{\text{SF}_6}$  with reasonable certainty. Despite the numerous vibrational modes available in  $\text{SF}_6$ , we also found it to be an inefficient quencher of  $\text{HCl}(v \leq 7)$ .<sup>5</sup>

Strong  $v$ -dependences are demonstrated by the  $\text{CO}$ ,  $\text{N}_2\text{O}$ , and  $\text{CF}_4$  rate constants for  $\text{DF}(2 \leq v \leq 4)$  relaxation yielding  $n$  values of 2.2–2.3 when fit using the power law expression. These are comparable to the  $n$  values obtained for quenching of  $\text{HF}(v)$  by  $\text{CO}_2$  ( $2.8 \pm 0.30$ ) and  $\text{N}_2\text{O}$  ( $3.0 \pm 0.3$ ). For  $\text{HF}(v)$  quenching, similar values of  $n$  apply to the highest levels,  $v = 5-7$ ; however, as shown in Table 5 for  $\text{DF}(v = 9-12)$  the  $v$ -dependence for  $\text{CO}_2$  is very weak and for  $\text{CO}$  and  $\text{N}_2$ ,  $k_{v,v-1}^{\text{Q}}$  appears to decrease at high  $v$ . Only  $\text{N}_2$  shows a high value of  $n$ , 6.6, which is, however, lower than the value, 8.4, shown in its relaxation of  $\text{HF}(v = 5-7)$ . The quenching of  $\text{DF}(v = 9-12)$  is characterized by small  $\Delta E_{V-V}$  values, which pass through zero in this energy regime for  $\text{CO}$  and  $\text{N}_2\text{O}$ . This strongly suggests that  $V-V$  exchange is important, even though the forms of the Lambert-Salter plots for  $\text{Q} = \text{N}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  are not wholly consistent with this view.

The contribution of  $V-V$  energy transfer in  $\text{DF}(v \leq 4) + \text{N}_2\text{O}$  was experimentally verified by the observation of emission from the  $\nu_3$  band of  $\text{N}_2\text{O}^\dagger$ . Similarly,  $\text{CO}_2$  ( $\nu_3$ )

emission was detected in relaxation studies of  $DF(v \leq 4)$ ; however, this emission overlapped the  $DF^{\dagger}$  emission, precluding rate measurements. Nonetheless, a significant relaxation probability for V-V energy transfer is implied, consistent with the smaller  $\Delta E_{V-V}$ 's. It should be pointed out that these observations do not rule out the possibility of energy transfer to combination bands such as  $N_2O (v_2 + v_3)$  which is nearly resonant in  $DF(v = 2)$  relaxation. This additional channel may also explain the relatively larger rate constants determined for  $Q = N_2O$  relative to  $CO$ , despite similar energy mismatches for low  $v$ .

The experimental evidence thus suggests a strong underlying  $v$  effect coupled with a  $\Delta E_{V-V}$  effect which partially cancel each other for several  $DF(v) + Q$  reactions but not for  $HF(v)$ . Thus, the observed  $v$  dependence for the relaxation of high vibrational states of  $DF$  by  $Q = CO, CO_2$ , and  $N_2O$  is due to the partial cancellation of a strong  $v$  dependence by opposing  $\Delta E_{V-V}$  effects. However, the  $v$  and  $\Delta E_{V-V}$  effects reinforce each other for relaxation of  $HF(v)$  and lower  $v$ -levels of  $DF$  and may explain the unusually large  $n$  values determined from power law fits.

## SUMMARY AND CONCLUSIONS

Significant work was completed during this contract period pertaining to the vibrational relaxation of DF studied by infrared chemiluminescence using our fast-flow reactor. This work has resulted in three publications (see References 1-3) and several presentations (see References 51-53). The principal new results are summarized below:

1. Vibrational relaxation rate constants for  $DF(9 \leq v \leq 12)$  and  $HF(5 \leq v \leq 7) + HF(v = 0)$ ,  $DF(v = 0)$  in all combinations are independent of the magnitude or sign of the vibrational energy defect, indicating V-R,T energy transfer.

2. The vibrational relaxation mechanism for highly excited hydrogen halides appears to involve independent effects based on  $\Delta E_{V-V}$  and  $v$  which partially cancel in certain cases while reinforcing each other in other instances.

3. In general, similar relaxation probabilities are obtained for the vibrational relaxation of energetically comparable states of HF and DF.

4. No isotope effect is found in the energy disposal of the  $F + H_2/D_2$  reaction pair, consistent with classical dynamics. However, the  $H/D + F_2$  reaction pair has a significantly larger vibrational energy disposal into the DF product, as predicted by theory.

It is particularly encouraging that a large and consistent data base is being formed to describe vibrational relaxation processes involving diatomic molecules. However, fundamental energy transfer questions remain unanswered, awaiting a major theoretical attack on this problem. For example, it remains unclear why many of these relaxation processes exhibit pronounced  $v$  dependences, especially with collision partners having weak

intermolecular interactions. The comparison with experimental data obtained for other non-hydrogen halide excited diatomics is also somewhat puzzling, since these rate constants exhibit no clear  $v$  dependence and are two to three orders of magnitude slower.

In conclusion, the vibrational relaxation rate constants determined by this study are not only interesting from a fundamental standpoint but should also find practical use in the modelling of high power chemical lasers. Inferences concerning the relative importance of V-V and V,R-T energy transfer in the DF self-relaxation process are particularly significant in the context of these modelling efforts.

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TABLE 1  
Comparison of Initial Relative Vibrational Distributions  
of DF From F + D<sub>2</sub> + DF(v) + D

v =	1	2	3	4	<fv>	Method	Reference
0.29		0.67	1.00	0.66	0.65	Arrested Relaxation	32
0.15		0.52	1.00	0.59	0.67	Arrested Relaxation	33
0.31 ± 0.10		0.58 ± 0.09	1.00	0.80 ± 0.08	0.66	Chemiluminescence Mapping	27
0.24 ± 0.06		0.49 ± 0.07	1.00	0.70 ± 0.06	0.67	Fast Flow	This work

TABLE 2

Comparison of Initial Relative Vibrational State Distributions  
of DF from  $D + F_2 \rightarrow DF(v) + F$

v	<u>Experimental Method</u>		
	Measured Relaxation <sup>a</sup>	Chemiluminescence Mapping <sup>b</sup>	Fast Flow <sup>c</sup>
2	0.05	0	0
3	0.08	0	(0.01) <sup>e</sup>
4	0.10	0	(0.03) <sup>e</sup>
5	0.15	0	(0.07) <sup>e</sup>
6	0.15	0	0.14
7	0.41	0	0.22
8	0.59	0	0.48
9	0.84	0	1.00
10	1.00	0.10	0.73
11	0.63	1.00	0.51
12	0.24	0.58	0.15
13	<0.08	0.29	0.04
14	<0.06	d	0
$\langle \epsilon_v \rangle$	0.62	0.78	0.64

<sup>a</sup>Reference 26

<sup>b</sup>Reference 27

<sup>c</sup>This work

<sup>d</sup>DF(v>14) emission outside the range of the detector

<sup>e</sup>Estimated value from experimental spectra

TABLE 3

Measured Rate Constants,  $k_{V, v-1}^Q$ , Energy TransferProbabilities, P, and Vibrational Energy Defects,  $\Delta\epsilon_{V \rightarrow V'}$ .

$\underline{v}$	$\underline{\text{HF}(v) + \text{HF}}$		$\underline{\text{DF}(v) + \text{HF}}$		$\underline{P}$	$\underline{\Delta\epsilon_{V \rightarrow V'} (\text{cm}^{-1})}$	$\underline{v}$	$\underline{k_{V, v-1}^Q, 10^{-10} \text{ cm}^3 \text{ s}^{-1}}$	$\underline{P}$	$\underline{\Delta\epsilon_{V \rightarrow V'} (\text{cm}^{-1})}$
	$k_{V, v-1}^Q, 10^{-10} \text{ cm}^3 \text{ s}^{-1}$	$\underline{\text{HF}(v) + \text{HF}}$	$k_{V, v-1}^Q, 10^{-10} \text{ cm}^3 \text{ s}^{-1}$	$\underline{\text{DF}(v) + \text{HF}}$						
5	1.4	0.47	2.6	0.86		-663	9	2.6		-1739 566 <sup>a</sup>
6	2.9	0.96	3.6	1.17		-819	10	3.6		-1819 404 <sup>a</sup>
7	4.5	1.45	4.5	1.44		-973	11	4.5		-1900 243 <sup>a</sup>
			5.5	1.72			12	5.5		-1980 82 <sup>a</sup>

$\underline{v}$	$\underline{\text{HF}(v) + \text{DF}}$		$\underline{\text{DF}(v) + \text{DF}}$		$\underline{P}$	$\underline{\Delta\epsilon_{V \rightarrow V'} (\text{cm}^{-1})}$	$\underline{v}$	$\underline{k_{V, v-1}^Q, 10^{-10} \text{ cm}^3 \text{ s}^{-1}}$	$\underline{P}$	$\underline{\Delta\epsilon_{V \rightarrow V'} (\text{cm}^{-1})}$
	$k_{V, v-1}^Q, 10^{-10} \text{ cm}^3 \text{ s}^{-1}$	$\underline{\text{HF}(v) + \text{DF}}$	$k_{V, v-1}^Q, 10^{-10} \text{ cm}^3 \text{ s}^{-1}$	$\underline{\text{DF}(v) + \text{DF}}$						
5	1.5	0.51	2.0	0.67		392	9	2.0		-684
6	2.5	0.84	2.4	0.79		236	10	2.4		-764
7	3.8	1.24	3.3	1.07		82	11	3.3		-845
			4.3	1.37			12	4.3		-925

<sup>a</sup> $\Delta\epsilon_{V \rightarrow V'}$  assumes  $\Delta v = -2$  for  $\text{DF}(v)$ .

TABLE 4

Quenching Rate Constants  $k_{v,v-1}^Q$ , Energy Transfer Probabilities  $P$ , and Vibrational Energy Defects  $\Delta E_{v-v}$  for DF ( $v = 2-4$ ) + HF, DF, CO,  $N_2O$ ,  $CF_4$ , and  $SF_6$

Q		v= 2	3	4
HF	$k_{v,v-1}^Q$ ( $10^{-12}$ cm <sup>3</sup> s <sup>-1</sup> )	5.0	17	33
	$P_{v,v-1}$	0.018	0.062	0.12
	$\Delta E_{v-v}$ (cm <sup>-1</sup> )	-1147	-1236	-1323
DF	$k_{v,v-1}^Q$ ( $10^{-12}$ cm <sup>3</sup> s <sup>-1</sup> )	14	17	27
	$P_{v,v-1}$	0.052	0.063	0.10
	$\Delta E_{v-v}$ (cm <sup>-1</sup> )	-92	-181	-268
CO	$k_{v,v-1}^Q$ ( $10^{-12}$ cm <sup>3</sup> s <sup>-1</sup> )	0.84	1.9	4.0
	$P(10^{-2})$	0.30	0.67	1.4
	$\Delta E_{v-v}$ (cm <sup>-1</sup> ) <sup>a</sup>	672	583	496
$N_2O$	$k_{v,v-1}^Q$ ( $10^{-12}$ cm <sup>3</sup> s <sup>-1</sup> )	8.9	24	42
	$P(10^{-2})$	2.7	7.1	12
	$\Delta E_{v-v}$ (cm <sup>-1</sup> ) <sup>b</sup>	591	502	415
$CF_4$	$k_{v,v-1}^Q$ ( $10^{-12}$ cm <sup>3</sup> s <sup>-1</sup> )	(0.22) <sup>e</sup>	0.53	1.1
	$P(10^{-2})$	0.065	0.15	0.32
	$\Delta E_{v-v}$ (cm <sup>-1</sup> ) <sup>c</sup>	1532	1443	1356
$SF_6$	$k_{v,v-1}^Q$ ( $10^{-12}$ cm <sup>3</sup> s <sup>-1</sup> )	--	--	0.19
	$P(10^{-2})$	--	--	0.045
	$\Delta E_{v-v}$ (cm <sup>-1</sup> ) <sup>d</sup>	--	--	1692

<sup>a</sup>Based on  $\nu = 2143$  cm<sup>-1</sup>

<sup>d</sup>Based on  $\nu = 947$  cm<sup>-1</sup>

<sup>b</sup>Based on  $\nu = 2224$  cm<sup>-1</sup>

<sup>e</sup>Bracketed value is less accurate

<sup>c</sup>Based on  $\nu = 1283$  cm<sup>-1</sup>

TABLE 5

Quenching Rate Constants  $k_{v,v-1}^Q$ , Energy Transfer Probabilities  
 $P$ , and Vibrational Energy Defects  $\Delta E_{V-V}$  for DF( $v = 9-12$ )  
 +  $N_2$ , CO,  $CO_2$ , and  $N_2O$

Q		$v=$ 9	10	11	12
$N_2$	$k_{v,v-1}^Q$ ( $10^{-11}$ cm <sup>3</sup> s <sup>-1</sup> )	(0.59) <sup>e</sup>	1.5	2.3	4.2
	$P_{v,v-1}$	(0.020)	0.049	0.074	0.13
	$\Delta E_{V-V}$ (cm <sup>-1</sup> ) <sup>a</sup>	-106	-186	-267	-347
CO	$k_{v,v-1}^Q$ ( $10^{-11}$ cm <sup>3</sup> s <sup>-1</sup> )	(17)	22	18	13
	$P_{v,v-1}$	(0.56)	0.71	0.57	0.41
	$\Delta E_{V-V}$ (cm <sup>-1</sup> ) <sup>b</sup>	80	0	-81	-161
$CO_2$	$k_{v,v-1}^Q$ ( $10^{-11}$ cm <sup>3</sup> s <sup>-1</sup> )	(21)	24	26	30
	$P_{v,v-1}$	(0.59)	0.66	0.71	0.80
	$\Delta E_{V-V}$ (cm <sup>-1</sup> ) <sup>c</sup>	-126	-206	-287	-367
$N_2O$	$k_{v,v-1}^Q$ ( $10^{-11}$ cm <sup>3</sup> s <sup>-1</sup> )	(35)	27	27	26
	$P_{v,v-1}$	(0.97)	0.74	0.73	0.69
	$\Delta E_{V-V}$ (cm <sup>-1</sup> ) <sup>d</sup>	-1	-81	-162	-242

<sup>a</sup>Based on  $\nu = 2329$  cm<sup>-1</sup>

<sup>b</sup>Based on  $\nu = 2143$  cm<sup>-1</sup>

<sup>c</sup>Based on  $\nu = 2349$  cm<sup>-1</sup>

<sup>d</sup>Based on  $\nu = 2224$  cm<sup>-1</sup>

<sup>e</sup>Bracketed values are less accurate

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